THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

# CORROSION PROBLEMS IN THE PULP AND PAPER INDUSTRY

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## INTRODUCTION

Some months ago, The Institute of Paper Chemistry, in co-operation with a large manufacturer of pipe and fittings, undertook to develop information regarding the nature and the extent of the corrosion problems which exist in the pulp and paper industry. The work was preliminary in character in that it was not aimed immediately at solutions to the existing problems. Its objective was rather to determine the feelings of the industry itself regarding the seriousness of the problems and the desirability of a concerted experimental attack which might aid in providing more information regarding the proper use of existing materials and, in some cases, better materials. From that standpoint, it is considered desirable to present the information which has been gathered. Therefore, it is the object of this paper to discuss, not answers to corrosion problems, but rather the opinions of a considerable number of pulp and paper manufacturers regarding the most serious corrosion problems with which they are currently faced.

For the purpose at hand, 79 manufacturers of pulp and/or paper (all members of The Institute of Paper Chemistry) were selected as providing a representative cross section of the industry, both geographically and as regards the various pulping and papermaking processes currently in commercial practice. These manufacturers were contacted by letter, in which the situation was outlined and in which they were asked specifically if they felt a comprehensive co-operative study of corrosion in the industry was feasible. Of the 78 manufacturers who replied, 56 indicated that they believed that such a study would be worth while and that they would be willing to co-operate actively in it. Five were undecided either as to the necessity for an experimental study or their participation in it, and 17 did not feel that a corrosion study was necessary. It is interesting to note that the greater part of the 17 negative replies came from companies with only papermaking operations (no pulping), in which the corrosion difficulties are comparatively less severe.

This response to the original letter indicated quite definitely that there are serious corrosion problems in the industry which, at least to the knowledge of the men who must deal with them, are unsolved. The next step taken was to contact again the 56 interested manufacturers, this time asking them to describe in detail their most troublesome corrosion problems, to indicate the materials or means used in attempted alleviation of the difficulties, and the success or lack of success attendant thereto. Thirty-one replies to this second request have been received thus far and it is these which constitute the basis of this paper.

The 31 above-mentioned manufacturers operate the following numbers of pulp and paper mills:

13 sulfite pulp mills,

11 alkaline pulp mills,

10 groundwood pulp mills, and

50 paper mills.

Since no mention of corrosion problems specific to groundwood pulping was made, no discussion is needed. The corrosion problems encountered in the other listed categories are discussed separately.

SULFITE PULPING

In the production of wood pulp by the sulfite process, wood chips are subjected to digestion by a sulfur dioxide-bisulfite solution at elevated temperature and pressure. The so-called cooking acid may contain from 6 to 10% total sulfur dioxide, of which 1 to 2% are combined as the sulfite of calcium, magnesium, sodium, or ammonia; it may exist in the digesters at temperatures up to 280° F. and pressures up to 90 lb./sq. in. gage. During the acid preparation cycle, lower values of concentration, temperature, and pressure exist. It is these strongly acid solutions which give rise to the most serious corrosion problems in the sulfite industry.

Almost all sulfite digesters are constructed of ordinary steel, with acidproof brick linings. Provided the lining is maintained properly, they give satisfactory service. Older plants still use considerable lead or lead-lined equipment for handling sulfur dioxide gas and cooking acid solutions at atmospheric temperature and pressure.

For handling both gas and liquor at elevated temperature and pressure, the preferred material is one of the stabilized stainless alloys such as Types 316 or 317. Almost all mills have completely replaced the bronze or brass fittings and lines previously used with these alloys, and many are using them instead of lead at low temperatures and pressures. Other stainless alloys find considerable use, although it has generally been found that the nonstabilized types are unsatisfactory. Several mills report good service from alloys of the 29% chromium-9% nickel type. One has had considerable success with an alloy little used in the industry, Type 329, and reports that it can be field-welded without carbon precipitation and subsequent corrosion near the weld.

Although the general feeling is quite definitely one of satisfaction with the stabilized stainless alloys, one of the interesting phases of this survey has been in pointing up the several instances of failure and inadequacy of these alloys. Almost without exception, these failures can be traced to conditions which might be expected to destroy the passive surface and to prevent its regeneration. Pure sulfur dioxide solutions, although strongly reducing, apparently do not attack the stainless steels appreciably. However, under conditions of continuous exposure to the cooking acid solutions with no chance for periodic cleansing or reoxidation, severe corrosion is apt to occur. An example cited by one manufacturer is the gasket surface at a flange in a stainless line. The line itself shows little corrosion, whereas the gasket surface rapidly develops severe pitting. Abrasive conditions in the presence of the reducing solutions are also cited, as are air-cooking acid interfaces, and the presence of appreciable concentrations of sulfur trioxide. The industry knows of no solution to these problems.

Also associated with cooking acid preparation is the combustion of sulfur and the cooling of the hot burner gas thus formed. One specific problem involves the introduction of molten sulfur to the burners for which no metal appears to stand up satisfactorily. In one instance, Type 316 stainless steel gives about 2 months' service. Another involves handling of the hot gas, which may be at a temperature of about 2300° F. as it leaves the burner. For the hot gas, cast iron is most commonly used but is a source of difficulty. One mill has tried Types 302 and 347 rolled plates without success, and is now trying Type 316 cast stainless and nickel cast iron.

## ALKALINE PULPING

The alkaline pulping processes depend, as the name implies, upon the action of alkaline solutions for the delignification of wood. In the soda process, the cooking liquor is a solution of sodium hydroxide, usually containing some sodium carbonate. In the kraft, or sulfate, process, the cooking chemical is a mixture of sodium hydroxide and sodium sulfide, with some sodium carbonate and sodium sulfate usually present. Since the processes are essentially similar and since corrosion is usually much more severe in kraft pulping, attention will be directed to that process.

Kraft cooking liquors may contain from 10 to 12% total alkali, with a "sulfidity" (percentage of total alkali present as sulfide) of from 15 to 30%. The pressure in the digester may be as high as 130 lb./sq. in. with a temperature up to 350° F. After digestion, the "black liquor," now containing large quantities of dissolved organic matter, is separated from the pulp by washing, concentrated to 55-60% total solids by multiple-effect evaporation, and burned. The sodium carbonate-sodium sulfide smelt from the furnace is dissolved in water to form "green liquor," which is then causticized with lime to regenerate the pulping solution ("white liquor") used in the digesters. Make-up chemical to the system is usually solid sodium sulfate, which is added to the concentrated black liquor immediately before the furnace. Corrosion difficulties are experienced throughout the whole cooking and recovery cycle.

In contrast to the situation in sulfite pulping, there is no general similarity in the problems encountered in the various mills. In some cases, the greatest problem is in the digesters and in the dilute black liquor system. Others find particular difficulty with the hot concentrated black liquor and still others find the causticizing system most troublesome. In most of the older mills, the original materials of construction were steel and cast iron. These materials have been found wanting in many instances, and have been or are being replaced in the particular locations of most difficulty. In these replacements and in new installations, a variety of materials is being used. Most mills believe that excellent performance would be demonstrated by Types 316 and 317 stainless alloys, but feel that extensive use of these alloys cannot be justified economically and that other, cheaper, materials should prove adequate.

Kraft digesters, for the most part, have been of steel construction. Corrosion has been sufficiently severe to make other materials attractive and several stainless-clad digesters are in operation. In the multiple-effect black liquor evaporators, it has become fairly common practice to use tubes of Type 302 or 304 stainless alloys in the first two effects, since these effects usually handle the hottest and most concentrated liquor. One mill has gone to Type 316 or 317 stainless tubes for these effects and for the piping system between the evaporators and the furnace.

Since these liquors are strongly alkaline, nickel alloys should be of advantage, and the survey indicates that they are being used considerably, particularly in causticizing and white liquor systems. Nickel-copper-iron alloys of the Ni-Resist type are satisfactory in many cases, and steels or cast irons containing 3-6% nickel are finding considerable use. For the evaporation of caustic solutions, usually saturated with salt (from brine electrolysis), tubes of high nickel alloys such as Monel metal are fairly standard. For either white, green, or black liquors, 3-6% chromium alloys appear to be completely unsatisfactory, but the 12-14% chromium alloys stand up well in some cases.

In the combustion of black liquors, the flue gases from the furnace contain high percentages of water vapor, the usual amount of carbon dioxide, some sulfur dioxide, and large quantities of sodium sulfate dust. It is necessary to recover as much of the dust as possible in scrubbers, precipitators, or the like; this usually necessitates the cooling of the gases below the dew point. The liquid phase which forms is acid and very corrosive. Although it is presumed that stainless steel would meet this requirement satisfactorily, most mills have not found this solution feasible and the problem is a serious one.

Practically all the producers of kraft pulp concerned in this survey feel that they have a serious corrosion problem. The difficulties are more specific than general and there is some indication that they may be regional--the problem appears to be most severe in the Pacific Northwest. This is presumed to be associated with the wood species pulped and with their chemical composition and behavior. As with most industrial problems, satisfactory solutions must be based on economic as well as technical considerations.

## BLEACHING

The bleaching of chemical wood pulps is almost universally conducted with chlorine and chlorine compounds. In a typical multi-stage bleaching operation, chlorine gas or chlorine water (a solution of chlorine in water) is used in the first stage. This is followed by a caustic extraction stage using sodium hydroxide, which in turn is followed by one or more oxidation stages with calcium or sodium hypochlorite. Chlorine dissolves in water with the formation of equimolal quantities of hypochlorous and hydrochloric acids and, thus, the medium in the first stage has a very low pH (usually less than 2) and a high chloride ion concentration. The hypochlorite solutions used in the latter stages are well on the alkaline side (pH about 11 to 12) and also contain high chloride ion concentrations.

It is well known that the handling of hydrochloric acid solutions presents a very difficult corrosion problem. The problem appears to be equally difficult when hypochlorous acid is also present, and no completely satisfactory construction materials are known for these solutions. Although the attack becomes progressively less severe with sodium and with calcium hypochlorite, these solutions also present many difficulties.

For handling moist chlorine gas, chlorine water, or pulp slurries containing dissolved chlorine, the nonmetallic materials appear to be most satisfactory. Glass and acidproof tile stand up well, but are rather limited in practical application. Although several mills discussed experience with glass pumps and piping, this material is distinctly limited because of its mechanical properties. Tile is used extensively for lining bleach tanks and bleachers of various designs. Hard rubber, rubber-lined pipe, and rubber-covered equipment usually show good performance and are used extensively where feasible--for example, in washers for the chlorinated stock. Haveg is being utilized to some extent, and Saran is being investigated. For the acid bleach solutions, some failures with Saran have been reported. Considerable interest is evidenced in protective coatings of various sorts, of which chlorinated rubber paint is an example, but performance has been poor.

Although the nonmetallic materials are used wherever possible, the need for satisfactory metals is acute. Brass, bronze, steel, cast iron, and the stainless steels are, of course, completely unsuitable. Among the best of the metals are lead, Hastelloy C, and the 14% silicon cast irons (particularly Durichlor), but all the materials have serious limitations. Lead creeps badly, is subject to serious erosion, and exhibits only fair corrosion resistance. Hastelloy C often shows a relatively short life, is costly, and is difficult to handle. The high silicon cast irons are costly, brittle, and difficult to handle but, in the few instances mentioned, appear to show good corrosion resistance. All in all, a more satisfactory metal for this service is badly needed.

Although steel is generally considered to be a satisfactory material for handling liquid chlorine and dry chlorine gas, several comments indicate some difficulties in such systems. The difficulties may be largely traceable to the presence of moisture, which may have backed up into the chlorine piping from the bleach-making system. Several mills use Hastelloy C chlorine valves where this possibility exists.

It has been mentioned that the problem is much less severe in the case of the alkaline hypochlorite stages but is still troublesome. Sodium hypochlorite solutions are considerably more corrosive than those of calcium hypochlorite, the difference apparently lying in the presence or formation of insoluble sludges with the calcium bleach which coat the equipment and protect the original material. For either solution, steel, black iron, and wrought iron are generally unsatisfactory, but cast iron is considerably more resistant and is used in many instances, particularly with calcium hypochlorite. Transite finds considerable use, a popular combination being Transite pipe with cast iron fittings. Rather surprisingly, several of the stainless alloys show fairly good corrosion resistance, although their performance appears to be spotty and there are marked differences of opinion regarding their suitability. Hastelloy C and the 14% silicon cast irons stand up well but suffer from the drawbacks mentioned above. Saran is considerably better in alkaline hypochlorites than in acid chlorine solutions; a relatively new Saran-lined steel tubing is interesting.

One rather serious problem which exists around bleach plants is the general corrosion and rusting of the exteriors of piping, equipment, and structural steel. During much of the bleaching and washing of the pulp, the slurries may be exposed to the room and small quantities of chlorine gas are liberated. The chlorine, in the high humidity air which usually exists, is very corrosive to iron and steel. Examples can be cited where even stainless steel had failed from exterior corrosion. The problem is not confined to chlorine, but is present as well in sulfite pulping operations where sulfur dioxide may escape, and to a lesser extent throughout the mills. Many protective coatings have been and are being investigated, with results which range, in the words of one manufacturer, "from indefinite in most cases to downright poor in several."

## PAPERMAKING

Although the products of papermaking run the gamut from facial tissue to bond to wrapper to board, the general nature and sequence of processing operations are remarkably similar. Wood pulp, cotton rags, reclaimed waste paper, or cellulose from other minor sources, either separately or in combination, are reduced to a fibrous suspension, further bleached or deinked if necessary, and "refined" in a beater or other refining engine. In the refining operation, the fibers are subjected to mechanical action which leads to the development of strength and other desirable characteristics in the finished sheet. During or after refining, the furnish is dyed, if necessary, sized and fillers are added. The furnish is then screened, diluted as required, and fed to a continuously operated paper machine which converts the dilute aqueous suspension into a finished dry sheet.

With a few specific and notable exceptions, the corrosion problems assocated with papermaking are not of the severe nature encountered in pulping and bleaching. They are, nonetheless, important in the successful operation of the plant. In many instances, the necessity for extreme cleanliness in the product is as important in corrosion considerations as is the life of the equipment involved.

If, as is often the case, bleaching is conducted in the paper mill, the problems are the same as those discussed above and need not be considered further. Other specific problems arise with certain more or less specialized operations which require the use of sulfuric acid, hydrochloric acid, or other specific chemicals; these problems are often difficult but are not common to the industry as a whole.

One severe corrosion difficulty common to most of the industry arises in connection with sizing. Sizing may be done in the beater or later in the system. The most common sizing material is rosin, which is added as a mildly alkaline emulsion and offers no corrosion difficulty. The size is then precipitated with alum, which is added in an aqueous solution varying in concentration from 10 to 50%. The alum solutions are acid and difficult to handle. Copper, brass, iron, and steel are unsatisfactory as container materials. Lead is used extensively, but gives only fair service. Rubber appears to be reasonably satisfactory, except in a comparatively few instances. The reports on Type 316 stainless steel are confusing and contradictory. The few reported instances of the use of the 14% silicon cast irons indicate that they stand up well, but emphasize again the shortcomings of the materials. One mill has adopted the dry feeding of solid alum to the machine chest.

For the effective precipitation of the size on the fiber, it is necessary that sufficient alum be added to adjust the entire furnish to the acid side. This gives rise to the most generally experienced and most serious corrosion problem in papermaking. The condition of the furnish as it is fed to the paper machine varies with the particular mill and with the grade being run, but pH values range from 4.0 to 6.5 for sized sheets, at temperatures from 40 to 140° F. Although these conditions are not severe, the combination of product quality and equipment life dictates the use of materials other than iron and mild steel for much of the paper mill system.

Beaters, jordans, and other refining engines are for the most part constructed of steel, although many mills cite the rapid deterioration of all or portions of the refiners. Wooden and copper-lined beater tubs are quite common. Stock chests are, for the most part, tile lined. Stock and white-water piping may be copper, bronze, Transite, rubber lined, wood or wood lined, or Type 302, 304, or 316 stainless steel. Of these, it is the consensus of opinion that the stainless steels are the only truly satisfactory materials, but economic considerations preclude their use in many instances.

Choice among the various piping materials listed depends primarily upon the particular operating conditions. Copper and bronze are reasonably satisfactory in the higher pH range; Transite has a very limited use; wood or wood-lined pipe is difficult to install and maintain, and contributes to the slime control difficulties.

Conditions at the wet end of the paper machine parallel those in the stock piping. Headboxes, screens, stock inlets, white-water trays, and the like are constructed from a variety of materials, of which stainless and stainless-clad steels are most satisfactory. Brass and bronze are used extensively around the paper machine, but show considerable tendency for dezincification and destannification if the pH is low. Monel metal gives good service in many cases. Again, a considerable interest in the development of more satisfactory lining and coating materials is noted.

In mills producing high brightness papers particularly, rust and scale from water lines, steam lines, and the like may cause as much difficulty as dirt from the actual papermaking equipment. Again the problem is both economic and technical: how can this source of difficulty be controlled without recourse to the premium-priced alloys?

## GENERAL

The discussion above has been limited for the most part to problems specific to the pulp and paper industry. Other problems, no less serious in many instances, but more general, could be cited. Among these are corrosion in fresh-water lines, in water-treating operations, in boilers, steam lines and condensate return systems, and by atmospheric exposure. These problems will not be discussed in this paper.

## SUMMARY AND CONCLUSIONS

This report discusses in some detail the more important corrosion problems encountered in the pulp and paper industry. The difficulties specific to sulfite pulping, alkaline pulping, bleaching, and papermaking are discussed separately. Some of the conditions are so severe that even the most resistant materials are found wanting. For the most part, however, materials reasonably satisfactory from the corrosion standpoint are available, but in many instances mechanical shortcomings or high cost make the development of other materials extremely desirable.

For the most part, the very severe conditions encountered in sulifte pulping are satisfactorily met by the stabilized 18-8 stainless alloys. These alloys are generally satisfactory also in alkaline pulping but, in many instances, are difficult to justify economically. The problems encountered in bleaching wood pulp cannot be met satisfactorily with the presently used metallic materials.

In illustration of a difficult but not unduly severe problem, the paper mill stock and white-water systems are cited. Here the mildly acid conditions and moderately elevated temperatures preclude the use of iron and steel, and no other completely satisfactory material except the costly stainless steels is available. The provision of suitable materials for such services at moderate cost would fill a pressing need in the industry.

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